A RELATION BETWEEN ORTHOBARIC DENSITIES. PART II.

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The writer has derived in his foregoing paper[1] the following relation between orthobaric densities,

$$\psi = RT \ln V_g/V_l = A(1/(V_l - E) - 1/(V_g - E)) \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

where ψ denotes the internal heat of vaporization of hypothetical infinitesimal molecules, while A and E denote characteristic constants for individual substance, and V_l and V_g the molecular volume of liquid and vapour respectively. There have been given 21 cases of actual calculations to prove validity of equation (1). In the present work 22 more substances have been taken. Some of them which are provided with full data of orthobaric densities have been treated just in the same manner as before. For the others, of which only vapour tension and liquid density are given, the vapour density was calculated from vapour tension applying gas law below boiling point, and for those substances whose vapour densities only are given in a certain range of temperature, liquid densities were estimated by Cailletet-Mathias' rule from the vapour densities and a few known data of liquid densities. The calculations have been done with following 22 substance; carbon dioxide,[2] nitrous oxide, ammonia, sulphur dioxide, phosgene, n-pentane, n-hexane, di-isopropyl, n-heptane, di-isobutyl, fluorobenzene, bromobenzene, iodobenzene, chloroform, carbon disulphide, methyl formate, methyl propionate, methyl isobutylate, ethyl acetate, ethyl propionate, propyl acetate, and acetone. In this paper, however, abridged data[3] are shown to save the space.

In the following tables Q_M, Q_z, D_l and D_g denote $RT \ln \frac{V_g}{V_l}$, $A\left(\frac{1}{V_l - E} - \frac{1}{V_g - E}\right)$, and densities of liquid and vapour respectively.

(1) *J. Chem. Soc. Japan*, **47** (1926), 587; this journal, **1** (1926), 189.

(2) By Cailletet-Mathias' data, while in the previous paper by those of Amagat.

(3) Full data will be published in the *Journal of the Chemical Society of Japan* in Japanese.

TABLE 1. Carbon dioxide.

t°C	D_l	D_g	Q_M	Q_z
−23.0	0.998	(0.0475)	1514	1495
− 2.2	(0.898)	0.1040	1179	1179
15.9	0.796	(0.1726)	878	881
25.0	(0.685)	0.2543	587	585
28.9	(0.608)	0.3118	400	407

Critical temperature=31.0°C,[1] A=35270, E=21.1.
(Cailletet and Mathias, *J. Phys.*, (2) **5** (1886), 549).
Parenthesis in the table show numbers computed by empirical equations given by the observers.

TABLE 2. Nitrous oxide.

t°C	D_l	D_g	Q_M	Q_z
−23.5	(1.017)	0.0413	1590	1597
−12.2	(0.964)	0.0566	1471	1470
− 1.5	(0.907)	0.0785	1321	1330
9.2	(0.838)	0.1066	1157	1159
19.8	0.758	(0.1476)	953	949
25.4	(0.690)	0.1782	803	795

Crit. temp.=36.5°C,[2] A=56770, E=8.89.
(Cailletet and Mathias, ibid.)
Parenthesis in the table show numbers computed by empirical equations given by the observers.

TABLE 3. Ammonia.

t°C	D_l	D_g	Q_M	Q_z
−50	*1.4241	*2550	3322	3316
−20	*1.5033	* 612	3026	3026
+10	*1.6006	* 205.0	2731	2727
40	*1.7251	* 82.8	2409	2407
78.7	0.5120	0.0322	1935	1943
121.3	0.3831	0.1024	1035	1071

Crit. temp.=132.9°C,[3] A=47490. E=9.98.
Numbers with asterisks express the specific volume given by Osborne and Van Dusen[4]; while the others are the densities obtained by Berthoud.[5]

(1) Cardoso and Bell. *J. chim. phys.*, **10** (1912), 497; Landolt, "Tabellen," 5 ed., p. 258.
(2) Cardoso and Arni, *J. chim. phys.*, **10** (1912), 504; Landolt, "Tabellen," 5 ed., p. 262.
(3) Cardoso and Giltay, *J. chim. phys.*, **10** (1912), 514; Landolt, "Tabellen," 5 ed. p. 255.
(4) *Bur. Stannds Bull.*, **14** (1917), 414; "Tables Annuales," **5** (1925), 20.
(5) *J. chim. phys.*, **16** (1918), 429.

TABLE 4. Sulphur dioxide.

t°C	D_l	D_g	Q_M	Q_z
7.3	(1.4162)	0.00624	3024	3018
21.7	1.3757	(0.0105)	2857	2861
37.5	(1.3306)	0.0169	2696	2697
58.2	(1.2653)	0.0310	2443	2463
82.4	1.1845	(0.0525)	2202	2186
120.45	1.0166	(0.1268)	1628	1629
140.8	0.8690	(0.2250)	1131	1142
154.9	0.6483	0.4017	407	425

Crit. temp. = 157.15°C,[1] $A = 77740$, $E = 19.54$.
(Cailletet and Mathias, *Compt. rend.*, **102** (1887), 1563; Landolt, "Tabellen," 5 ed., p. 281.)
Parenthesis denote the numbers obtained by interpolation.

TABLE 5. Phosgene.

t°C	D_l	D_g	Q_M	Q_z
60.3	1.2780	0.0193	2779	2777
100.1	1.1655	0.0493	2347	2347
130.0	1.0637	0.0305	1975	1973
170.6	0.8219	0.2424	1077	1081
181.6	0.7089	0.3276	697	715

Crit. temp. = 187°C,[2] $A = 116200$, $E = 28.09$.
(Patterno and Mazzuccuelli, *Gazz. Chim.*, **50** (1920), 38; "Tables Annuales," **5** (1925), 20.

TABLE 6. n-Pentane.

t°C	D_l	D_g	Q_M	Q_z
0	0.64539	(0.0007844)	3645	3642
40	0.6 62	0.003361	3234	3239
80	0.5624	0.01012	2821	2817
120	0.5107	0.0250	2358	2355
160	0.4394	0.0591	1727	1745
197.1	0.2560	0.2090	190	203

Crit. temp. = 197.2°C, $A = 21690$, $E = 53.62$.
(Young, *Sci. Proc. Roy. Dublin Soc.*, **12** (1910), 374).
Parenthesis denote the data calculated from vapour pressure.

(1) Cardoso and Bell, loc. cit.; Landolt, "Tabellen," 5 ed., p. 261.
(2) Critical temperature mentioned here as well as those hereafter, if not otherwise described, are the data given by the observer of the densities.

TABLE 7. n-Hexane.

t°C	D_l	D_g	Q_M	Q_z
0	0.6769	(0.0002319)	4332	4324
30	0.6505	(0.0008523)	3999	3999
60	0.6221	0.002488	3656	3668
90	0.5918	0.00585	3325	3337
120	0.5588	0.01202	3000	2998
150	0.5207	0.02299	2627	2627
180	0.4751	0.04228	2179	2194
210	0.4124	0.07899	1584	1624

Crit. temp.=234.8°C, A=276000, E=64.48.
(Young, ibid.)
Parenthesis denote the numbers calculated from vapour pressure.

TABLE 8. Di-isopropyl.

t°C	D_l	D_g	Q_M	Q_z
0	0.67948	(0.0003876)	4055	4040
30	0.6525	(0.001311)	3742	3741
60	0.6243	0.003479	3437	3439
90	0.5931	0.007782	3129	3125
120	0.5589	0.01555	2799	2798
150	0.5197	0.02825	2450	2439
180	0.4705	0.05216	1981	2000
226.5	0.2967	0.1848	470	499

Crit. temp.=227.35°C, A=264400, E=62.58.
(Young, ibid.)
Parenthesis denote the numbers calculated from vapour pressure.

TABLE 9. n-Heptane.

t°C	D_l	D_g	Q_M	Q_z
30	0.6951	(0.0003115)	4628	4620
60	0.6491	(0.001015)	4279	4273
90	0.6218	0.002703	3926	3931
120	0.5926	0.006075	3580	3585
150	0.5598	0.01222	3217	3226
180	0.5232	0.02242	2838	2834
210	0.4793	0.04005	2384	2414
240	0.4177	0.07446	1759	1789

Crit. temp.=266.85°C, A=340500, E=75.90.
(Young, ibid.)
Parenthesis denote the numbers calculated from vapour pressure.

TABLE 10. Di-isobutyl.

t°C	D_l	D_g	Q_M	Q_z
90	0.6328	0.002239	4074	4072
120	0.6046	0.005219	3714	3725
150	0.5732	0.01070	3348	3361
180	0.5383	0.01959	2984	2979
210	0.4970	0.03484	2552	2551
240	0.4434	0.06223	2003	2017
270	0.3482	0.1387	1047	1092

Crit. temp. = 276.8°C, A = 381000, E = 86.98.
(Young, ibid.)

TABLE 11. Fluorobenzene.

t°C	D_l	D_g	Q_M	Q_z
0	1.04653	(0.0001180)	4935	4935
30	1.0104	(0.0004908)	4598	4598
60	0.9744	(0.001503)	4288	4284
90	0.9366	0.003846	3967	3971
120	0.8955	0.008347	3654	3650
150	0.8519	0.01629	3329	3326
180	0.8037	0.02911	2989	2983
210	0.7480	0.04968	2605	2601
240	0.6789	0.08403	2131	2140
270	0.5739	0.1535	1424	1456

Crit. temp. = 286.55°C, A = 221600, E = 46.87.
(Young, ibid.)
Parenthesis denote the numbers calculated from vapour pressure.

TABLE 12. Bromobenzene.

t°C	D_l	D_g	Q_M	Q_z
50	1.4546	(0.0001321)	5979	5979
80	1.4142	(0.0004722)	5620	5643
110	1.3729	(0.001307)	5299	5320
140	1.3293	(0.003021)	4999	4999
170	1.2847	0.006562	4649	4681
200	1.2385	0.01209	4354	4371
230	1.1876	0.02079	4046	4040
260	1.1310	0.03427	3706	3687

Crit. temp. = 397°C, A = 312100. E = 55.73.
(Young ibid.)
Parenthesis denote the numbers calculated from vapour pressure.

TABLE 13. Iodobenzene.

t°C	D_l	D_g	Q_M	Q_z
80	1.7391	(0.0002018)	6357	6357
110	1.6932	(0.0006307)	6014	6024
140	1.6453	(0.001622)	5684	5697
170	1.5972	(0.003542)	5384	5384
200	1.5470	0.007278	5040	5063
230	1.4941	0.01295	4749	4745
260	1.4384	0.02200	4430	4423

Crit. temp.=448°C, A=367100, E=5957.
(Young, ibid.)
Parenthesis denote the numbers calculated from vapour pressure.

TABLE 14. Chloroform.

t°C	D_l	D_g	Q_M	Q_z
−53.6	1.62580 (T)	0.00001340 (D)	5120	5115
−51.0	1.62075 (I)	0.00001639 (D)	5079	5079
−45.0	1.60988 (T)	0.00002593 (D)	5005	5002
−37.2	1.59511 (T)	0.00004563 (D)	4907	4903
−17.5	1.5559 (I)	0.0001667 (D)	4645	4645
− 6.2	1.53811 (T)	0.0003095 (D)	4517	4535
[illegible]	1.51700 (I)	0.0005281 (R)	4403	4406
[illegible]	1.50175 (Ty)	0.0007596 (R)	4315	4316
16.00	1.49739 (T.H.)	0.0008174 (R)	4290	4291

Crit. temp.=260.0°C,(1) A=167800, E=40.60.

(D): From vapour pressures given by Drucker and Kangro, *Z. physik. Chem.*, **90** (1915), 513.
(R): From vapour pressures given by Rex, *Z. physik. Chem.*, **55** (1906), 358.
(T): Timmermanns, *Sci. Proc. Roy. Dublin Soc.*, **13**, 326; "Tables Annuales," **3** (1914), 10.
(Ty): Tyrer, *J. Chem. Soc.*, **99** (1911), 871.
(H): Herz and Rathmann, *Chem. Zt.*, **146**, 1417; "Tables Annuales," **3** (1914), 10.
(T.H.): Mean of the densities given by (T) and (H).
(I): Interpolated from the data given in the above papers as well as the followings. Isnardi, *Z. Physik*, **9** (1922), 158; Faust, *Z. physik. Chem.*, **79** (1912), 97; Dolezalek and Schulze, *Z. physik. Chem.*, **83** (1913), 67; Flecker and Tyrer, *J. Chem. Soc.*, **103** (1913), 52; Tyrer, *J. Chem. Soc.*, **104** (1914), 2534.

(1) Sajetschewsky, *Kiewer. Univers. Unters.*, 1878, No. 4 & No. 8; Landolt, "Tabellen" 5 ed., p. 257.

TABLE 15. Carbon disulphide.

t°C	D_l	D_g	Q_M	Q
−14.1	1.31324	0.00030170	4301	4306
− 3.06	1.29680	0.00051030	4209	4209
+ 8.26	1.28004	0.00079920	4121	4128
16.37	1.26807	0.0010964	4058	4059
22.44	1.25909	0.0013642	4011	4011
57.08	1.20484	0.0040642	3732	3736
78.82	1.17021	0.0072888	3558	3554
99.24	1.13583	0.011671	3389	3389
130.48	1.07964	0.021660	3117	3137

Crit. temp. = 273.05°C,[1] $A = 149500$, $E = 23.22$

Densities of vapour were given by Battelli[2] for the whole range of temperature. Densities of liquid have been estimated by Cailletet-Mathias' rule. Densities of liquid from 0° to 35° have been found from the following papers: Bugarsky, *Z. physik. Chem.*, **71** (1910), 705; Dawson, *J. Chem. Soc.*, **97** (1910), 1041; Tyrer, *J. Chem. Soc.*, **97** (1910), 2620; De Leeuw, Dissert. Amsterdam, **1910**, 22; "Tables Annuales," **1** (1912), 11.

TABLE 16. Methyl formate.

t°C	D_l	D_g	Q_M	Q_z
0	1.00319	(0.000687)	3956	3956
30	0.9598	0.002291	3638	3636
60	0.9133	0.006039	3324	3323
90	0.8634	0.01350	3002	3001
120	0.8070	0.02688	2659	2654
150	0.7403	0.05063	2256	2259
180	0.6521	0.09434	1762	1754
210	0.4857	0.2188	765	803

Crit. temp. = 214.0°C, $A = 125200$, $E = 28.21$.

(Young, ibid.)

Parenthesis denote the numbers calculated from vapour pressure.

(1) Battelli, *Mem. Torino*, (2) **42** (1891), 1; ibid., **41** (1890), 1; Landolt, "Tabellen," 5 ed., p. 281.
(2) Ibid.

TABLE 17. Methyl propionate.

t°C	D_l	D_g	Q_M	Q_z
70	0.8537	0.002331	4026	4026
100	0.8137	0.005741	3678	3678
130	0.7705	0.01214	3326	3324
160	0.7221	0.02356	2936	2945
190	0.6657	0.04320	2518	2532
220	0.5938	0.07812	1988	2011
250	0.4655	0.1675	1063	1110

Crit. temp.=257.4°C, A=222400, E=47.99.
(Young, ibid.)

TABLE 18. Methyl i-butylate.

t°C	D_l	D_g	Q_M	Q_z
90	0.8069	0.003361	3957	3957
120	0.7680	0.007628	3604	3606
150	0.7248	0.01533	3244	3237
180	0.6767	0.02869	2847	2847
210	0.6200	0.05141	2392	2403
250	0.5021	0.1218	1473	1519

Crit. temp.=267.55°C, A=270600, E=58.29.
(Young, ibid.)

TABLE 19. Ethyl acetate.

t°C	D_l	D_M	Q_M	Q_z
10	0.9127	(0.000213)	4707	4700
40	0.8762	(0.000840)	4327	4328
70	0.8376	0.002561	3950	3964
100	0.7972	0.006158	3608	3609
130	0.7533	0.01314	3245	3246
160	0.7033	0.02577	2847	2853
190	0.6441	0.04751	2398	2415
210	0.5944	0.07128	2037	2029
249	0.3839	0.2288	537	570

Crit. temp.=250.1°C, A=221300, E=49.40.
(Young, ibid.)
Parentesis denote the numbers calculated from vapour pressure.

TABLE 20. Ethyl propionate.

t°C	D_l	D_g	Q_M	Q_z
90	0.8077	0.002674	4122	4127
120	0.7692	0.00620	3767	3766
150	0.7267	0.01292	3390	3391
180	0.6795	0.02469	2986	2986
210	0.6243	0.04464	2534	2550
240	0.5501	0.08230	1938	1974
270	0.4018	0.1957	777	831

Crit. temp. = 272.9°C, $A = 281600$, $E = 58.29$.

TABLE 21. Propyl acetate.

t°C	D_l	D_g	Q_M	Q_z
90	0.8079	0.002457	4184	4184
120	0.7702	0.005760	3826	3824
150	0.7297	0.01195	3459	3460
180	0.6835	0.02268	3068	3065
210	0.6301	0.04115	2623	2628
240	0.5586	0.07576	2038	2067
270	0.4333	0.1661	1031	1093

Crit. temp. = 276.2°C, $A = 283700$, $E = 58.70$

TABLE 22. Acetone

t°C	D_l	D_g	Q_M	Q_z
−83.4	0.90321 (T)	0.000000317	5605	5558
−78.0	0.900 (S)	0.000000608	5511	5511
−63.3	0.88150 (T)	0.00000287	5269	5254
−50.0	0.8670 (K)	0.00000967	5058	5058
−37.2	0.85337 (T)	0.00002490	4897	4894
−30.0	0.8463 (K)	0.00004056	4807	4799
−13.0	0.83105 (D)	0.0001185	4587	4620
− 6.2	0.81943 (T)	0.0001768	4479	4486
5	0.8081 (B)	0.0002985	4365	4365
10	0.8038 (B)	0.0003793	4310	4301

Crit. temp. = 234.4°C,(1) $A = 152700$, $E = 36.80$.

D_g was calculated from vapour tensions given by Drucker and Kangro, ibid.

(T): Timmermanns, ibid.
(K): Körber, *Ann. Phys.*, **37** (1912), 1014; "Tables Annuales," **3** (1914), 10.
(S): Stern, *Z. physik. Chem.*, **81** (1913), 441.
(D): Dutich, *Verh. K. Akad. Wet. Amsterdam*, **11**, 44; "Tables Annuales" **3** (1914), 10.
(B): Bramley, *J. Chem. Soc.*, **109** (1916), 434.

(1) Galizine, *Wied. Ann.*, **41** (1890), 620.

Table 1—22 show that the concordance of RT ln $\frac{V_g}{V_i}$ with A $\left(\frac{1}{V_i - E} - \frac{1}{V_g - E}\right)$ is excellent except at temperatures immediately near the critical temperature. Moreover, as vapour densities are calculated from vapour tensions at low temperatures, it is evident that following equation (2), which was derived from equation (1) as a vapour tension formula in the previous work, agrees with experimental data.

TABLE 23. Summary of constant E.

Substance	$E_{calc.}$	$E_{add.}$	$V_{P=\infty}$	V_K	E/V_K
Hydrogen	4.20	—		70.3	0.060
[illegible]en	9.68	8.0		74.5	0.130
Ni[illegible]	12.8	—		90.1	0.142
Argo[illegible]	10.3	—		75.2	0.137
Carbon dioxide	21.1	21.6		94.8	0.223
Nitrous oxide	8.87	—		107	0.083
Ammonia	9.98	—		72.0	0.139
Sulphur dioxide	19.54	—		125.0	0.156
Phosgene	28.09	28.9		192.7	0.146
n-Pentane	53.62	54.0		310	0.173
i-Pentane	53.8	54.0		308	0.175
n-Hexane	64.48	65.0		367	0.176
Di-isopropyl	62.58	65.0		357	0.175
Heptane	75.90	76.0		427	0.178
n-Octane	87.0	86.9		491	0.177
Di-isobutyl	86.98	86.9		482	0.180
Benzene	41.51	41.5		256	0.162
Hexamethylene	52.6	52.3		308	0.171
Fluorobenzene	46.87	46.7		271	0.173
Chlorobenzene	50.15	51.0		308	0.163
Bromobenzene	55.73	55.4		323	0.172
Iodobenzene	59.57	59.7		351	0.170
Chloroform	40.60	37.7		—	—
Carbon tetrachloride	44.32	46.9		276	0.161
Carbon disulphide	23.22	—		202	0.115
Stannic chloride	58.43	—		351	0.166
Methyl formate	28.21	25.9		172	0.164
Methyl acetate	37.8	37.0		228	0.166
Methyl propionate	47.99	48.0		282	0.169
Methyl butylate	59.2	59.0		340	0.174
Methyl i-butylate	58.29	59.0		339	0.169
Ethyl formate	37.8	37.0		229	0.165
Ethyl acetate	49.40	48.0		286	0.173
Ethyl propionate	58.29	59.0		344	0.168
Propyl formate	46.5	48.0		285	0.163
Propyl acetate	58.7	59.0		346	0.170
Ethyl ether	50.0	47.0	49.9 (Tas.)	286	0.174
Acetone	36.80	34.0	35.6 (Tas.)	—	—
Methyl alcohol	24.40	26.7	23.1 (Tam.)	118	0.207
Ethyl alcohol	37.8	37.7	33.6 (Tam.)	167	0.226
Propyl alcohol	48.6	48.7		220	0.221
Acetic acid	30.0	—		171	0.175

Additive constants.

(H) = −0.54	(F) =4.35	Double bond = − 4.6
(C) = 12.1	(Cl) =2×(F)= 8.70	Hydroxyl group = 16.2
(O) = 4.0	(Br) =3×(F)=13.05	Ring formation = −13.7
	(J) =4×(F)=17. 4	

$$\ln P = \ln \frac{RT}{V_l} - \frac{1}{RT}\frac{A}{V_l - E} \qquad (2)$$

Table 23 is the summary of the values of E hitherto obtained for 42 substances. In this work, besides that of carbon dioxdie shown in Table 1, the constants of carbon tetrachloride and benzene were recalculated by more careful computation, and are shown in the table.

E_{calc} in the second column is the values directly calculated. E_{add} in the third column which show pretty good agreement with E_{calc} were calculated from additive constants shown at the bottom of the table. These constants consist of 6 fundamental numbers, and enable us to calculate constant E for 33 different substances. The values for C and H have been estimated from the data for normal hydrocarbons. The constant for a double bond was calculated assuming the benzene contains three of them. The group -CO-O- in esters was regarded to consist of two normal oxygen and a double bond. The constants for Cl are approximately the same for $COCl_2$, $CHCl_3$, CCl_4 etc.. It is interesting that the constants of halogenobenzenes are very accurately expressed by assuming to their constants 1, 2, 3, 4, times of that of fluorine respectively. $V_{p=\infty}$ in the fourth column denotes the volumes of liquids extrapolated to infinitely large pressure. The data adopted are of Tammann[1] and of Tashiro[2], the latter being very close to E_{calc} in the case of ethyl ether and acetone. In the fifth, there are shown critical volumes calculated from data given in Landolt-Börnstein's table. Values of E/V_k in the last column are almost universally constant for normal liquids, the mean value of which being 0.170.

In the previous work, it was derived a reduced equation from equation (1), taking into account that the ratio $\frac{T_k}{\sqrt{AP_k}}$ are universally constant as well as $\frac{E}{V}$. The total summary of values for the constant A and $\frac{T_k}{\sqrt{AP_k}}$ are given in Table 24. This table shows that the constancy of the value $\frac{T_k}{\sqrt{AP_k}}$ for normal liquids is satisfactory, the following value having been obtained for their mean through the total data:

$$\frac{T_k}{\sqrt{AP_k}} = 0.1765.$$

(1) *Ann. Phys.* **87** (1912), 975.
(2) *Bulletin of the Institute of Physical and Chemical Research* (in Japanese), **6** (1927), 105.

TEBLE 24. Summary of constant A.

Substance	A	$\frac{T_k}{\sqrt{AP_k}}$
Hydrogen	3958	0.148
Oxygen	18160	0.162
Nitrogen	17520	0.164
Argon	17440	0.165
Carbon dioxide	35270	0.189
Nitrous oxide	56770	0.154
Ammonia	47490	0.176
Sulphur dioxide	77740	0.175
Phosgene	116200	—
n-Pentane	216900	0.176
i-Pentane	204300	0.174
Hexane	276000	0.177
Di-isopropyl	264400	0.176
Heptane	340500	0.178
Octane	355900	0.180
Di-isobutyl	381000	0.180
Benzene	218200	0.174
Hexamethylene	249700	0.175
Fluorobenzene	221600	0.178
Chlorobenzene	292700	0.175
Bromobenzene	312100	0.179
Iodobenzene	367100	0.178
Chloroform	167800	0.176
Carbon tetrachloride	232500	0.172
Carbon disulphide	149500	0.166
Stannic chloride	307600	0.176
Methyl formate	125200	0.179
Methyl acetate	173700	0.178
Methyl propionate	222400	0.179
Methyl butylate	276700	0.179
Methyl i-butylate	270600	0.179
Ethyl formate	174000	0.178
Ethyl acetate	221300	0.180
Ethyl propionate	281600	0.179
Propyl formate	232700	0.173
Propyl acetate	283700	0.179
Ethyl ether	185600	0.181
Acetone	152700	0.169
Methyl alcohol	78950	0.205
Ethyl alcohol	105900	0.200
Propyl alcohol	143500	0.197
Acetic acid	151100	0.202

The writer wishes to express his sincere thanks to Prof. M. Katayama for his kind guidance throughout the present study.

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THE VISCOSITY OF LIQUIDS ABOVE THEIR BOILING POINTS. PART IV.[1]

By Toshizo TITANI.

Received July 22, 1927. Published August 28, 1927.

In part II of this paper we have obtained the following equations expressing the relations between the molecular fluidity Φ defined as $\frac{1}{\eta . V^{\frac{1}{3}}}$ and molecular volume V or temperature T:

$$\Phi = K(V^{\frac{1}{3}} - B^{\frac{1}{3}}) \quad \cdots\cdots(1),$$

$$\Phi_K - \Phi = C(T_K - T)^{\frac{1}{3}} \quad \cdots\cdots(2),$$

where K and C are arbitrary constants and Φ_K, T_K critical constants. As regards the specific fluidity Φ_1 referred to one gram, we have obtained exactly the same form of equations, which contain specific volume V_1 and constants K_1, C_1 and Φ_{1K} instead of K, C aud Φ_K. In the present paper some properties of the constants in the above equations will be considered.

First of all the constant B, an effective molecular volume, in equation (1) is of additive nature.[2] In the following table the observed values of B are compared with those calculated by adding respective elementary parts :—

C=6.9, H=5.1, O=7.5, Cl=20.0, F=10.5, double linking=3.0, iso-grouping=0.

TABLE 1. Additivity of constant B.

Substance	Formula	$B_{obs.}$	$B_{calc.}$	Δ
Pentane	C_5H_{12}	95.5	95.7	+0.2%
Isopentane	C_5H_{12}	96.1	95.7	−0.4
Hexane	C_6H_{14}	112.6	112.8	+0.2
Heptane	C_7H_{16}	129.9	129.9	0
Octane	C_8H_{18}	147.9	147.0	−0.6
Methyl-formate	$C_2H_4O_2$	52.0	52.2	+0.4
Ethyl-formate	$C_3H_6O_2$	69.6	69.3	−0.4
Propyl-formate	$C_4H_8O_2$	86.8	86.4	−0.5
Methyl-acetate	$C_3H_6O_2$	68.9	69.3	+0.6
Ethyl-acetate	$C_4H_8O_2$	86.1	86.4	+0.3
Propyl-acetate	$C_5H_{10}O_2$	104.2	103.5	−0.7
Methyl-propionate	$C_4H_8O_2$	85.0	86.4	+1.7
Ethyl-propionate	$C_5H_{10}O_2$	102.9	103.5	+0.6
Methyl-butyrate	$C_5H_{10}O_2$	102.7	103.5	+0.8
Methyl-isobutyrate	$C_5H_{10}O_2$	102.9	103.5	+0.6
Ethyl ether	$C_4H_{10}O$	85.7	86.1	+0.5
Carbon tetrachloride	CCl_4	88.9	86.9	−2.2
Benzene	C_6H_6	82.2	81.0	−1.3
Fluorobenzene	C_6H_5F	85.5	86.4	+1.0
Chlorobenzene	C_6H_5Cl	94.1	95.9	+1.9
Acetic acid	$C_2H_4O_2$	54.0	52.2	−3.3
Carbon dioxide	CO_2	29.5	27.9	−5.4

(1) Part I, this journal, **2** (1927), 95; II, ibid., 161; III, ibid., 196.
(2) It was shown by Batschinski that the constant ω in his formula is also of additive nature. *Z. physik. Chem.*, **84** (1913), 643.

The constants K, C, B and Φ_K in equations (1) and (2) have been reduced by using critical constants from the standpoint of corresponding states. The results are shown in Table 2 and 3.

1). The constant B has a dimension of volume, so that it can be reduced by dividing it with the critical molecular volume V_K :—

$$b_r = \frac{B}{V_K}.$$

2). From the form of equations (1) and (2) it will easilly be seen that the constants K and C can be reduced as follows:

$$k_r = \frac{K.V_K^{\frac{3}{3}}}{\Phi_K},$$

$$c_r = \frac{C.T_K^{\frac{1}{2}}}{\Phi_K},$$

where T_K represents the critical temperature and Φ_K the critical molecular fluidity.

3). The dimension of viscosity η is equal to that of momentum divided by area and from the kinetic theory of gases the velocity v in the momentum may be considered to be proportional to $\sqrt{\frac{T}{M}}$ where T is absolute temperature and M the molecular weight so that :[1]

$$[\eta] = \frac{[\text{Momentum}]}{[\text{Area}]} = \frac{[M][v]}{[V]^{\frac{2}{3}}} = \frac{[M]^{\frac{1}{2}}[T]^{\frac{1}{2}}[R]^{\frac{1}{2}}}{[V]^{\frac{2}{3}}} \quad \cdots\cdots\cdots\cdots(3),$$

where V represents volume and R the gas constant.

Using the above relation, the constants K and C may also be reduced as follows:

$$k_r' = K.M.^{\frac{1}{2}}T_K.^{\frac{1}{2}}V_K^{\frac{1}{3}},$$

$$c_r' = \frac{CM^{\frac{1}{2}}T_K^{\frac{7}{6}}}{V_K^{\frac{1}{3}}}.$$

4). From equations (2) and (3) we obtain the following reduced form of the constant Φ_K,

$$\varphi'_{Kr} = \frac{\Phi_K M^{\frac{1}{2}}T_K^{\frac{1}{2}}}{V_K^{\frac{1}{3}}}$$

The reduced constants obtained above have actually been calculated for various substances and tabulated below together with the actual constants.

(1) This result has already been pointed out by K. Onnes, *Comm. Phys. Lab. Univ. Leiden*, 2 (1891).

As the values of Φ_K in k_r and c_r, those calculated from equations (1) and (2) have respectively been used.

TABLE 2. Actual constants.

Substance	K	B	C	Φ_K
Pentane	31.8	95.50	251	795.4
Isopentane	32.1	96.10	254	799.5
Hexane	25.4	112.6	219	702.6
Heptane	21.7	129.9	204	660.1
Octane	18.6	147.9	188	612.9
Methyl-formate	43.8	52.04	229	729.5
Ethyl-formate	34.0	69.60	218	696.1
Propyl-formate	27.5	86.82	202	649.3
Methyl-acetate	37.1	68.98	233	742.4
Ethyl-acetate	28.2	86.10	211	674.4
Propyl-acetate	23.8	104.2	196	630.0
Methyl-propionate	28.9	85.04	208	669.2
Ethyl-propionate	23.5	102.9	195	628.5
Methyl-butyrate	23.6	102.7	193	623.5
Methyl-isobutyrate	23.8	102.9	194	624.0
Ethyl ether	33.8	85.69	250	791.0
Carbon tetrachloride	20.4	88.88	147	470.7
Benzene	34.4	82.21	236	756.6
Fluorobenzene	28.8	85.51	200	647.3
Chlorobenzene	24.5	94.12	179	601.1
Acetic acid	(2250)	(0.8997)	(705)	(2291)
Bromine	(4400)	(0.2868)	(688)	(2273)
Carbon dioxide	(3060)	(0.669)	—	—

Note: Numbers in brackets represent quantities referred to one gram.

TABLE 3. Reduced constants.

Substance	k_r	$k'_r \times 10^{-4}$	b_r	c_r	$c'_r \times 10^{-4}$	$\varphi'_{Kr} \times 10^{-4}$
Pentane	1.84	3.98	0.308	1.08	2.34	2.16
Isopentane	1.85	3.95	0.312	1.08	2.34	2.16
Hexane	1.83	3.81	0.306	1.08	2.22	2.05
Heptane	1.83	3.80	0.304	1.09	2.22	2.04
Octane	1.82	3.74	0.302	1.09	2.32	2.12
Methyl-formate	1.82	4.17	0.302	1.08	2.43	2.24
Ethyl-formate	1.82	4.04	0.304	1.09	2.40	2.21
Propyl-formate	1.83	3.94	0.305	1.09	2.35	2.15
Methyl-acetate	1.82	4.39	0.303	1.09	2.57	2.35
Ethyl-acetate	1.82	3.99	0.301	1.09	2.40	2.20
Propyl-acetate	1.82	3.96	0.302	1.10	2.34	2.13
Methyl-propionate	1.82	4.10	0.302	1.09	2.41	2.21
Ethyl-propionate	1.81	3.89	0.299	1.09	2.32	2.12
Methyl-butyrate	1.82	3.92	0.302	1.10	2.33	2.13
Methyl-isobutyrate	1.83	3.90	0.304	1.09	2.30	2.10
Ethyl ether	1.83	4.12	0.304	1.08	2.42	2.24
Carbon tetrachloride	1.88	3.89	0.322	1.11	2.34	2.11
Benzene	1.86	4.58	0.321	1.11	2.76	2.28
Fluorobenzene	1.83	4.32	0.315	1.10	2.54	2.32
Chlorobenzene	1.83	4.41	0.306	1.08	2.57	2.38
Acetic acid	1.86	3.93	0.316	1.10	2.20	1.99
Bromine	1.95	4.29	0.339	1.08	2.67	2.47
Carbon dioxide	1.85	3.67	0.311	—	—	—
Mean	1.84	4.03	0.308	1.09	2.40	2.19

It will be seen from the above table that the respective constant becomes independent of the nature of the substance when it is expressed in reduced value.

Batschinski[1] also calculated the ratio $\frac{\omega}{V_{1K}}$ with various substances, where ω being the limiting volume in the rule proposed by him. This ratio should, according to him, as average be 0.307. Calculating the ratio with liquid carbon dioxide using the data actually measured by P. Phillips[2] near the critical point, it becomes 0.350. In the writer's case, using the same data, the ratio $\frac{B_1}{V_{1K}}$ is 0.311, which is only 1% greater than the average value 0.308.[3]

Reducing the respective quantities and constants in equations (1) and (2) by using the critical constants we have:

$$\frac{\phi}{\phi_K}=\frac{KV_K^{\frac{2}{3}}}{\phi_K}\left\{\left(\frac{V}{V_K}\right)^{\frac{2}{3}}-\left(\frac{B}{V_K}\right)^{\frac{2}{3}}\right\},$$

$$1-\frac{\phi}{\phi_K}=\frac{CT_K^{\frac{1}{2}}}{\phi_K}\left(1-\frac{T}{T_K}\right)^{\frac{1}{2}},$$

or for the sake of brevity,

$$\varphi_r=k_r(v_r^{\frac{2}{3}}-b_r^{\frac{2}{3}}) \quad \cdots\cdots(4),$$

$$1-\varphi_r=c_r(1-t_r)^{\frac{1}{2}} \cdots\cdots(5),$$

where φ_r, t_r etc. represent reduced quantities or constants.

Using relation (3) stated above, equations (1) and (2) may also be reduced as follows:

$$\frac{\phi.M.^{\frac{1}{2}}T_K^{\frac{1}{2}}}{V_K^{\frac{1}{3}}}=K.M.^{\frac{1}{2}}T_K.^{\frac{1}{2}}V_K^{\frac{1}{3}}\left\{\left(\frac{V}{V_K}\right)^{\frac{2}{3}}-\left(\frac{B}{V_K}\right)^{\frac{2}{3}}\right\},$$

$$\frac{\phi_K M^{\frac{1}{2}}T_K^{\frac{1}{2}}}{V_K^{\frac{1}{3}}}-\frac{\phi M^{\frac{1}{2}}T_K^{\frac{1}{2}}}{V_K^{\frac{1}{3}}}=\frac{CM^{\frac{1}{2}}T_K^{\frac{1}{2}}}{V_K^{\frac{1}{3}}}\left(1-\frac{T}{T_K}\right)^{\frac{1}{2}},$$

or

$$\varphi'_r=k'_r(v_r^{\frac{2}{3}}-b_r^{\frac{2}{3}}) \cdots\cdots(6),$$

$$\varphi'_{Kr}-\varphi'_r=c'_r(1-t_r)^{\frac{1}{2}} \cdots\cdots(7),$$

where φ'_r, k'_r etc. represent reduced quantities or constants which are different from φ_r, k_r etc.

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(1) loc. cit.

(2) P. Phillips, *Proc. Roy. Soc.*, (A) 87 (1912), 48.

(3) Cf. paragraph 2 part II of this paper cited above.

It has already been shown that the constants k_r, k'_r, c_r, c'_r, and φ'_{Kr} have universal values independent of the nature of the substance, so that above equations (4), (5), (6) and (7) may be considered to express the theory of corresponding states for molecular or specific fluidity.

Summary.

1. The constant B, the effective molecular volume, is additive.

2. The respective constant in the volume and temperature relations becomes independent of the nature of the substance when it is expressed in reduced form.

3. From the volume and temperature relations of the molecular fluidity the reduced equations of the following form have been obtained.

$$\varphi_r = k_r(v_r^{\frac{4}{3}} - b_r^{\frac{4}{3}}).$$

$$1-\varphi_r = c_r(1-t_r).^{\frac{4}{3}}$$

$$\varphi'_r = k'_r(v_r^{\frac{4}{3}} - b_r^{\frac{4}{3}}).$$

$$\varphi'_{Kr} - \varphi'_r = c'_r(1-t_r).^{\frac{4}{3}}$$

In conclusion, the writer wishes to express his cordial thanks to Prof. M. Katayama for his kind guidance.

July, 1927. The Institute of Physical and Chemical Research, Hongo, Tokyo.

SPECTROCHEMICAL STUDIES OF HYDROXYAZO-COMPOUNDS. PART IV.[1]

By Taku UEMURA and Shozo TABEI.

Received June 11 1927. Published August 28, 1927.

One of the authors[2] has already written on the tautomeric changes of some hydroxyazo-compounds and given them three different formulas according to their conditions.

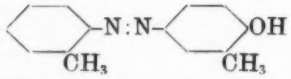
We have now studied more in detail about the influences of methyl-group on these hydroxyazo-compounds, for as we have seen in a previous

(1) Read before the Chemical Society of Japan, June 11, 1927.

(2) Uemura, Yokojima and Tan, This journal, **1** (1926), 260.
Uemura, Yokojima and Endo, ibid., **2** (1927), 10 & 48.

paper,[1] benzeneazo-p-cresol and p-nitrobenzeneazo-p-cresol have two absorption bands while the other compounds have but one. We have thought this was perhaps due to the methyl-group in the two above-mentioned hydroxyazo-compounds. In the present paper, we shall describe tolueneazo-cresols.

Experimental.

1. **o-Tolueneazo-o-cresol,**[2] 

The neutral solution of this compound is light yellow and by adding KOH-solution it becomes yellowish orange even a concentrated (0.5 N.) alkaline solution. We may assign A(azo)-form[3] to the neutral solution and R(red)-form[3] to the alkaline.

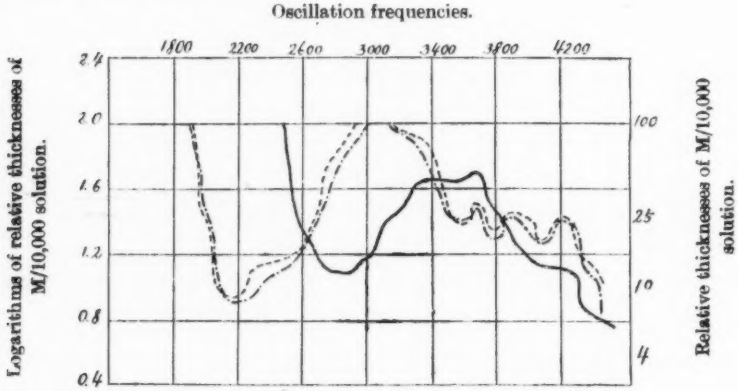
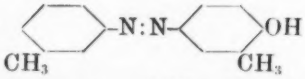


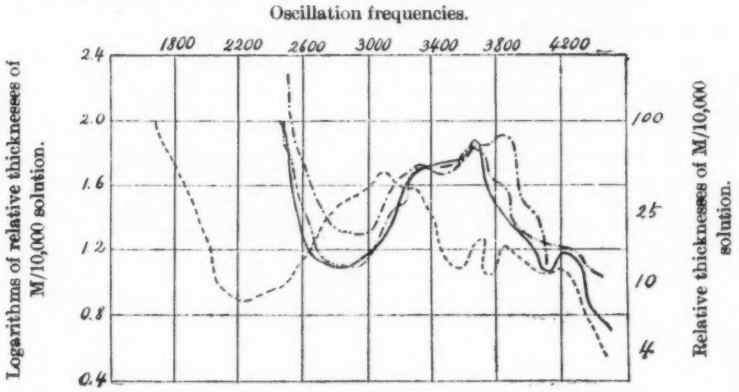
Fig. 1.

2. **m-Tolueneazo-o-cresol,**[4] 

The absorption curve of this compound (Fig. 2) is almost the same type as that of No. 1 compound. The colour change of this solution through alkali is also nearly the same as that of No. 1. When we compare the neutral solution curve of this compound with that of p-hydroxyazobenzene,[5]

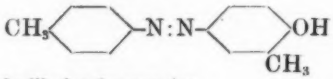
(1) This journal, **1** (1926), 262 & 265.
(2) Noelting and Werner, *Ber.*, **23** (1890), 3259.
(3) This journal, **1** (1926), 261.
(4) Jacobson, *Ann.*, **287** (1895), 185.
(5) This journal, **1** (1926), 262.

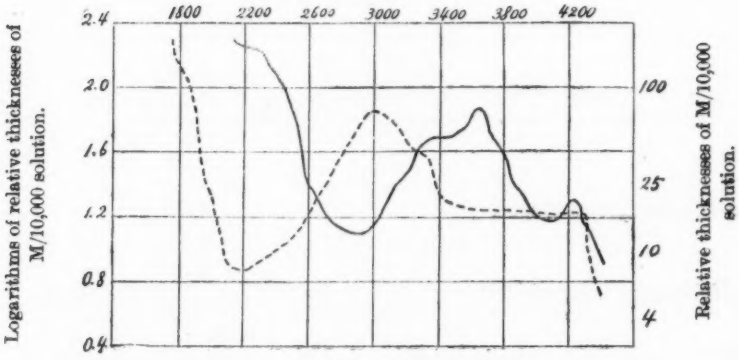
a considerably hyperchromic effect can be recognised, and the corresponding curve of benzeneazo-o-cresol[1] almost coincides with that of this compound. It seems to us that, although the methyl-group has a hyperchromic effect, yet it is still negligible against an already methylated compound.



2. m-Toluneazo-o-cresol. { ——— Neutral solution. - - - - 0.05 N. alkaline solution.
1 (Part I). p-Hydroxyazobenzene. —·—·— Neutral solution.
(Next report). Benzeneazo-o-cresol. —··—··— Neutral solution.

Fig. 2.

3. **p-Toluneazo-o-cresol,**[2] 

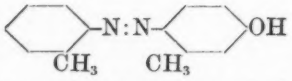


3. p-Toluneazo-o-cresol. { ——— Neutral solution. - - - - 0.05 N. alkaline solution.

Fig. 3.

(1) Details about this compound will appear in the next report.
(2) Noelting and Werner, *Ber.*, **23** (1890), 3261.

When this compound is neutral in solution, it is slightly yellow, but becomes yellowish orange by odding KOH. We may clearly recognise the bathochromic and hyperchromic influences due to an alkali in the absorption curve (Fig. 3).

4. o-Toluneazo-m-cresol,[1] 

The yellow neutral solution of this compound changes into a deeper shade by the addition of alkali and this bathochromic effect can also be observed in its absorption curve. As Fig. 4 shows, we can likewise conclude that the influence of the methyl-group is similar to No. 2 oompound. We may also see the position effect of the methyl-group in the cresol ring is very slight.

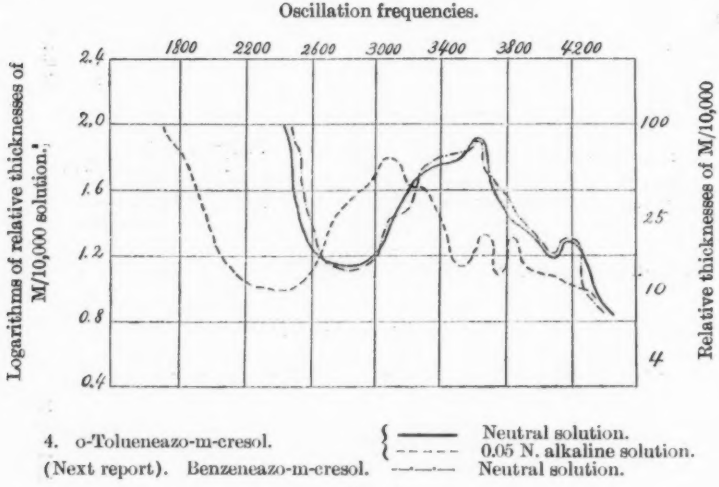
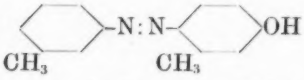
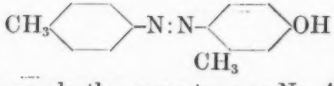


Fig. 4.

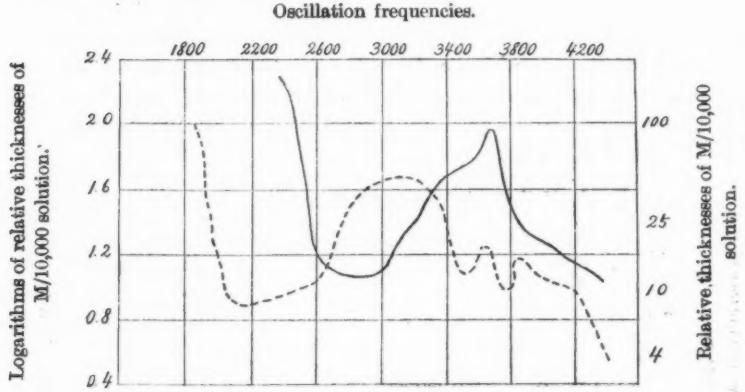
5. m-Toluneazo-m-cresol,[2] 

6. p-Toluneazo-m-cresol,[3] 

These two compounds have nearly the same type as No. 4 compound in their absorption curve (Fig. 5 and Fig. 6) of the neutral solution. We think

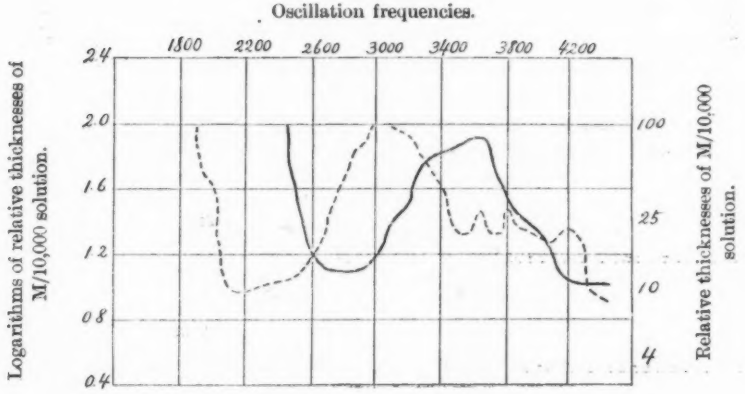
(1) Jacobson, *Ann.*, **287** (1895) 186.
(2) Jacobson, ibid., **287** (1895), 187.
(3) Jacobson, ibid., **287** (1895), 189.

this indicates the no position influence of the methyl-group in the toluene ring. As for the colour change, these compounds in solution are about the same as in No. 4 compound.



5. m-Toluneneazo-m-cresol. { ——— Neutral solution. - - - - - 0.05 N. alkaline solution.

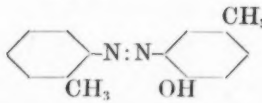
Fig. 5.



6. p-Toluneneazo-m-cresol. { ——— Neutral solution. - - - - - 0.05 N. alkaline solution.

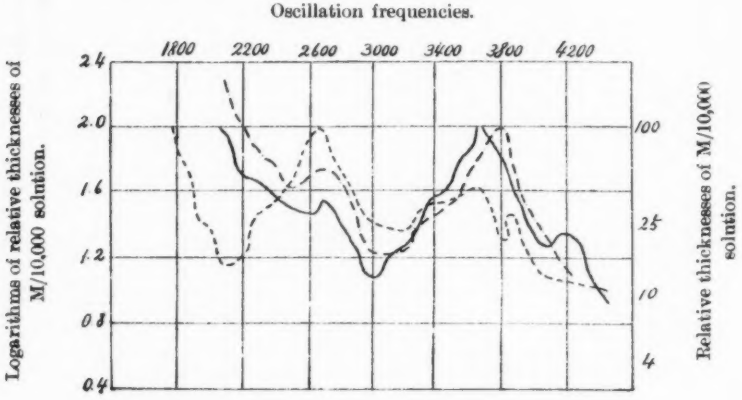
Fig. 6.

7. **o-Toluneneazo-p-cresol,**[1]



(1) Noelting and Werner, *Ber.*, 23 (1890), 3263.

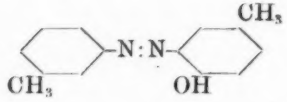
This compound has a hydroxyl-group in an ortho position with respect to the azo-group in cresol ring and has two absorption bands as is to be expected, and two bands more obvious can be also observed in the alkaline solution (Fig. 7). When we compare this absorption curve with that of benzeneazo-p-cresol,[1] the slight bathochromic and hyperchromic influences can be seen, and this is probably an effect of the methyl-group in the toluene ring. As the absorption curve of o-hydroxyazobenzene cannot yet been obtained, we are not here in a position perfectly to ascertain our point of issue like in the case of No. 2 compound.



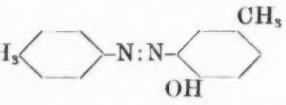
7. o-Tolueneazo-p-cresol. { ——— Neutral solution. ----- 0.05 N. alkaline solution.
3 (Part 1). Benzeneazo-p-cresol. —·—·— Neutral solution.

Fig. 7.

8. **m-Tolueneazo-p-cresol,**[2]



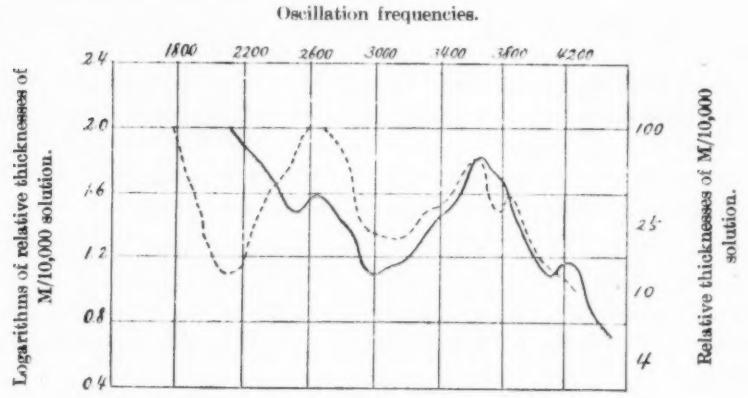
9. **p-Tolueneazo-p-cresol,**[3]



In these cases, we discover nearly the same absorption curves as that of No. 7 compound, that is, these compounds have two absorption bands in their solution. The bathochromic effect by the addition of alkali is remarkably observed in their absorption curves (Fig. 8 and Fig. 9). The neutral

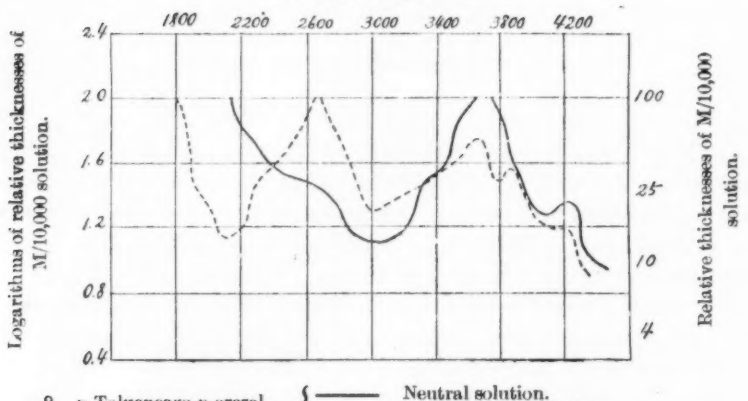
(1) This journal, 1 (1926), 263.
(2) Jacobson and Piepenbrink, *Ber.*, 27 (1894), 2703.
(3) Obtained from p-toluidine and p-cresol.

solutions of these two compounds are yellow like No. 7 compound and become orange when they are alkaline.



8. m-Toluneazo-p-cresol. { ——— Neutral solution. - - - - - 0.1 N. alkaline solution.

Fig. 8.



9. p-Toluneazo-p-cresol. { ——— Neutral solution. - - - - - 0.1 N. alkaline solution.

Fig. 9.

Summary.

(1) Tautomeric transformations may occur when the neutral solution of these tolueneazo-cresols change into the alkaline.

(2) The dilute neutral solution of these compounds is generally yellow and becomes deep yellow or orange when the solution is alkaline.

(3) We can respectively give A(azo)- and R(red)-forms[1] to these tautomers.

(4) There is one absorption band when hydroxyl-group in cresol ring takes para-position with regard to the azo-group, and two bands when ortho-position.

(5) The methyl-group has a hyperchromic influence, but when added to an already methylated compound, it ceases to be effective in the absorption curve.

(6) So far as the present studies are concerned, the methyl-group does not specially represent its influence with regard to the position.

We should like to express our hearty thanks to Prof. Yuji Shibata of the Tokyo Imperial University for the interest he has taken in the progress of these experiments. We are also indebted to the Department of Education and the School for a financial grant received in the pursuance of this research.

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ON THE SO-CALLED DIETHYL DICYANOGLUTACONATE AND SOME OF ITS DERIVATIVES. II.

By Yoshiyuki URUSHIBARA.

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In the previous paper[2] on the same subject the author pointed out the incorrectness of the view hitherto held on the composition and constitution of the so-called diethyl dicyanoglutaconate and described some of its derivatives. The results which were not referred to then, and those obtained further by the continued investigation will be noted in this paper.

The starting substance of the investigation on the diethyl dicyanoglutaconate, the cyanacetic ester, has been always prepared by Noyes' method.[3] That this method produces the mixture of methyl and ethyl esters, and that this fact has no direct effect upon the results, were explained in a separate paper.[4]

In order to distinguish the so-called diethyl dicyanoglutaconate from the real diethyl dicyanoglutaconate, which is not known in its free state, the former is followed by the word " semihydrate " according to the composition, but it must be remembered that the half molecule of water can not be removed.

(1) loc. cit.
(2) This journal, 2 (1927), 26.
(3) *J. Am. Chem. Soc.*, 26 (1904), 1545.
(4) This jourual, 2 (1927) 143.

The mechanism of the formation and the yield of the diethyl sodio-dicyanoglutaconate. In the condensation of ethyl cyanacetate, chloroform, and sodium ethylate, the reaction producing the diethyl sodio-dicyanoglutaconate, the mixture is brought to violent boiling when it is heated on the water bath, whereby apparently causing the escape of chloroform and diminishing the yield of the product. In fact, if the reaction is moderated by avoiding violent boiling, the yield of purified sodium compound is better (60% of the theoretical amount) than that attained by Errera (40%).[1] But the yield is not improved, even if the less volatile iodoform is used. Addition of chloroform in excess seems also to be of no use. The calculated amount of chloroform is sufficient to bring the mass nearly to neutral reaction, and the quantity of separated sodium chloride is not too small. Hence, it is probable that a side reaction occurs between chloroform and sodium ethylate, yielding the orthoformic ester, which the more prevails over the desired reaction, when the more rapidly heat is applied.

On the other hand, that the orthoformic ester is at first produced from chloroform and three-fourth of the sodium ethylate, and then it is condensed with cyanacetic ester by the action of remaining sodium ethylate, seems to be suggested by the following facts: Chloroform, carbon tetrachloride, and ethyl trichloracetate, give all the same compound, triethyl orthoformate, by the action of sodium ethylate, while all these three substances give the same diethyl sodio-dicyanoglutaconate by the action of ethyl cyanacetate and sodium ethylate.[2]

An experiment was carried out on the condensation of orthoformic ester and cyanacetic ester by means of sodium ethylate, but such did not take place. Hence, in the condensation of chloroform, sodium ethylate, and cyanacetic ester, the portion changed into orthoformic ester is lost, the corresponding amount of cyanacetic ester taking no part in the reaction. By the use of excess of chloroform and sodium ethylate, the amount of excess being in the proportion of one molecule to three, an increased yield of diethyl sodio-dicyanoglutaconate referred to the amount of the cyanacetic ester was obtained (70% of the theoretical amount.)

The formation of the diethyl sodio-dicyanoglutaconate by the condensation of ethyl cyanacetate and ethyl trichloracetate by means of sodium ethylate. The condensation of diethyl malonate and ethyl trichloracetate by means of sodium ethylate gives the tetraethyl sodio-dicarboxyglutaconate,[3] the same compound that is formed by using chloroform instead of ethyl trichloracetate. With a somewhat hopeless

(1) *Ber.*, 31 (1898), 1241.
(2) *Ber.*, 35 (1902), 2881; and see under.
(1) Ruheman, *Ber.*, 29 (1896), 1017.

expectation of obtaining the triethyl dicyanoaconitate, the condensation of ethyl cyanacetate and trichloracetate was tried. But the experiment showed that the product was nothing but the diethyl sodio-dicyanoglutaconate. 0.4570 Gr. of the substance decreased in weight by 0.0557 gr. after dehydration at 120°. (Found: $H_2O=12.2$. $C_{11}H_{11}O_4N_2Na\cdot 2H_2O$ requires $H_2O=12.24\%$.) 0.2024 Gr. of the dehydrated substance gave 0.0528 gr. of Na_2SO_4. (Found: Na=8.5. The formula requires Na=8.9%.)

The triethyl sodio-dicyanoaconitate has the formula $C_{14}H_{15}O_6N_2Na.\frac{1}{2}H_2O$, which requires $H_2O=2.65$; Na=6.79%.)

Colour of the diethyl sodio-dicyanoglutaconate. In the previous paper it was shown that this substance was obtained in colourless state from iodoform. But sometimes the same reaction produced a dark reddish substance which was not easily freed from the colouring matter. The specimen prepared from ethyl trichloracetate was greenish yellow. At any rate this sodium compound accompanies some impurities in varying colours according to the condition of the reaction. And it is difficult to remove entirely these colouring matters by repeated recrystallisation. But when the sodium compound was recrystallised by using animal charcoal several times, it became nearly colourless.

Metallic derivatives of the diethyl dicyanoglutaconate. Various metallic derivatives are known, but as all of them were prepared from yellow sodium derivative, and the yellow colour is not characteristic of this compound, the colours of other metallic derivatives have been investigated.

Silver derivative. When a cold aqueous solution of silver nitrate is added to a cold aqueous solution of the sodium derivative, a gelatinous precipitate is formed, which on heating changes into have been powder.

Copper derivative. Freshly precipitated copper derivative is a pink-red voluminous substance, which soon changes into reddish brown powder. When ammonia is added to the well-washed reddish brown copper derivative, it changes into white precipitate, the supernatant liquid being slightly blueish.

Ammonium derivative. The double decomposition of the silver derivative of the diethyl dicyanoglutaconate and ammonium chloride gave an ammonium derivative with properties similar to those of the sodium derivative. This ammonium derivative precipitates the diethyl dicyanoglutaconate semihydrate on acidifying its aqueous solution. It possesses the formula $C_{11}H_{12}O_4N_2\cdot NH_3\cdot 2H_2O$, but loses one molecule of water on heating at 130°.

0.1388 Gr. of the substance dried in the desiccator gave 16.9 c.c. of N_2 at 9° and 756 mm. (Found: N=14.50. $C_{11}H_{12}O_4N_2\cdot NH_3\cdot 2H_2O$ requires N=14.53%). 0.1452 Gr. of the substance dehydrated at 130° gave 19.2 c.c. of N_2

at 13° and 760 mm. (Found: N=15.55. $C_{11}H_{12}O_4N_2 \cdot NH_3 \cdot H_2O$ requires N=15.50%.) This substance decomposed when heated at a higher temperature.

Ruhemann[1] abtained an ammonium derivative by dissolving the diethyl dicyanoglutaconate semihydrate in aqueous ammonia. His compound has the composition $C_{11}H_{12}O_4N_2 \cdot NH_3 \cdot \frac{1}{2}H_2O$ and melts and decomposes at 162–163°. This is probably the ammonium derivative of the diethyl dicyanoglutaconate *semihydrate*, and the half molecule of water comes from the mother substance.

Incomplete hydrolysis of the diethyl dicyanoglutaconate semihydrate. Complete hydrolysis gives the diethyl dihydroxy-dinicotinate (diethyl 2.6-dioxypyridine-3.5-dicarboxylate).[2] The author obtained the hydrobromide and the picrate of diethyl dicarbamylglutaconate by the hydrolysis of the bromine addition compound of diethyl dicyanoglutaconate semihydrate, and transformed the hydrobromide into the diethyl dihydroxydinicotinate. The experiments show that this diamide is formed intermediately during the direct hydrolysis of diethyl dicyanoglutaconate semihydrate by dilute hydrochloric acid.

The semihydrate was hydrolysed by boiling in dilute hydrochloric acid and dissolved in it. Prolonged boiling produces the ultimate product, i.e., diethyl dihydroxydinicotinate, which separates out in white crystals from the boiling liquid. Before the appearance of this substance the boiling was stopped and the solution was cooled. A cryslalline substance was obtained and it gave a picrate identical in melting point with the picrate of diethyl dicarbamylglutaconate (197°).

Trial of synthesizing the real diethyl dicyanoglutaconate. According to L. Claisen[3] the diethyl diacetylglutaconate is formed in a moderate yield when orthoformic ester and acetic anhydride are heated with an excess of acetoacetic ester, and in a good yield when the ethoxymethylene-acetoacetic ester is introduced into the alcoholic solution of sodioacetoacetic ester. In the latter case the sodium derivative is formed, and from it the free ester is botained by treating with acid.

The diethyl sodio-dicyanoglutaconate does not give the corresponding free ester, but the semihydrate. The mixture of ethyl cyanacetate, triethyl orthoformate, and acetic anhydride, in the proportion of 2 mols : 1 mol : 3 mols, was boiled for two hours and distilled in vacuo (ca. 20 mm.) until the temperature reached 120°. By treating there sidue of the distillation with an alcoholic sodium ethylate solution, the diethyl sodio-dicyanoglutaconate was obtained, and on acidifying its aqueous solution the diethyl

(1) *J. Chem. Soc.*, 73 (1898), 283.
(2) *J. Chem. Soc.*, 73 (1898), 284.
(3) *Ann.*, 297 (1897), 1.

dicyanoglutaconate semihydrate was precipitated. The formation of the diethyl sodio-dicyanoglutaconate probably owed to the presence of the real diethyl dicyanoglutaconate. But as it is possible that the ethoxymethylene-cyanacetic ester and cyanacetic ester were present in the residue and they produced the diethyl sodio-dicyanoglutaconate by the action of sodium ethylate, the formation of the real diethyl dicyanoglutaconate can not be insisted on.

The condensation of ethyl ethoxymethylene-cyanacetate and ethyl sodiocyanacetate. Another method for synthesizing such methenyl compounds consists in the condensation of ethoxymethylene compounds and the corresponding sodio-compounds. This method was applied to the synthesis of the diethyl sodio-dicyanoglutaconate. Soon after the addition of ethyl ethoxymethylenecyanacetate to ethyl sodiocyanacetate in absolute alcohol, a crystalline substance separated out. On acidifying the aqueous solution of this substance the diethyl dicyanoglutaconate semihydrate was precipitated, which was quite identical with the specimen synthesized from chloroform.

The application of Claisen's condensation has enabled the author to synthesize all of the nitrile-esters of the dicarboxyglutaconic acid and the details will be given in another paper.

Dimethyl sodio-dicyanoglutaconate and its derivatives.[1] By the condensation of methyl cyanacetate and chloroform by means of sodium methylate in methyl alcohol the corresponding methyl compound was formed. Recrystallised from methyl alcohol, it was obtained as nearly colourless glittering crystals, which has the composition $C_9H_7O_4N_2Na \cdot 2CH_3OH$, but easily loses a part of the alcohol of crystallisation. 0.5081 Gr. of the substance decreased by 0.1092 gr. on heating at 150–160°. (At a lower temperature the escape of the alcohol was incomplete.) (Found: $CH_3OH = 21.52$. $C_9H_7O_4N_2Na \cdot 2CH_3OH$ requires $CH_3OH = 21.77\%$.) 0.3319 Gr. of the substance freed from the alcohol of crystallisation gave 0.1159 gr. of Na_2SO_4. (Found: $Na = 9.83$. $C_9H_7O_4N_2Na$ requires $Na = 10.00\%$.) When this sodium compound is recrystallised from water and dried in the desiccator it contains about one molecule of water. 0.3821 Gr. of this substance decreased by 0.0265 gr. on heating at 150–160°. (Found: $H_2O = 6.94$. $C_9H_7O_4N_2Na \cdot H_2O$ requires $H_2O = 7.26\%$.)

By acidifying the hot aqueous solution of the dimethyl sodio-dicyanoglutaconate, yellow crystals of dimethyl dicyanoglutaconate semihydrate $C_9H_8O_4N_2 \cdot \frac{1}{2}H_2O$ were precipitated.

0.2383 Gr. of the substance dried at 100–110° gave 26.3 c.c. of N_2 at 16.5°

(1) Cf. this journal, **2** (1927), 145.

and 761 mm. (Found: N=12.85. $C_9H_8O_4N_2 \cdot \frac{1}{2}H_2O$ requires N=12.90%). This substance melts at 225° (corr.), is insoluble in absolute alcohol, methyl alcohol, benzene, and acetone even when boiled.

When bromine was added to the dimethyl dicyanoglutaconate semihydrate suspended in chloroform, the intermediate product was insoluble in this solvent and no distinct bromine addition compound was obtained. But the reaction proceeded in the same direction as in the case of the ethyl compound, which was ascertained as follows: After the addition of bromine the solid substance was collected and introduced into ether containing water. The white solid was dissolved in alcohol and the alcoholic solution of picric acid was added. At once a picrate precipitated, which proved to be the picrate of the dimethyl dicarbamylglutaconate.

0.1505 Gr. of substance gave 19.6 c.c. of N_2 at 15.5° and 751 mm. (Found: N=14.96. $C_9H_{12}O_6N_2 \, C_6H_2 \, (OH) \, (NO_2)_3$ requires N=14.80%.)

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